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(56) Documents Cited
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(54) Abstract Title
# Hydrogen separator

(57) A hydrogen separator includes a thin hydrogen permeable foil 16 of between 3 and 15 microns thick, bonded to and generally conforming to an undulating support structure 18 for example a wire mesh. The support structure is optionally coated with an inter-diffusion barrier prior to bonding. The disclosed method for bonding the foil to the support is by rolling. The support structure 18 has contact areas 20 and the foil only contacts the support at these points. This allows the foil to move in three dimensions in response to the thermal expansion of the support during use.

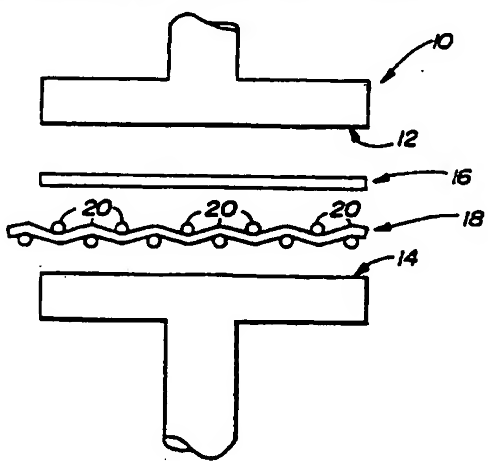


Fig-1

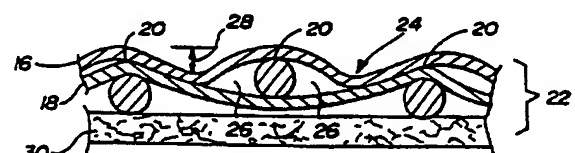


Fig-2

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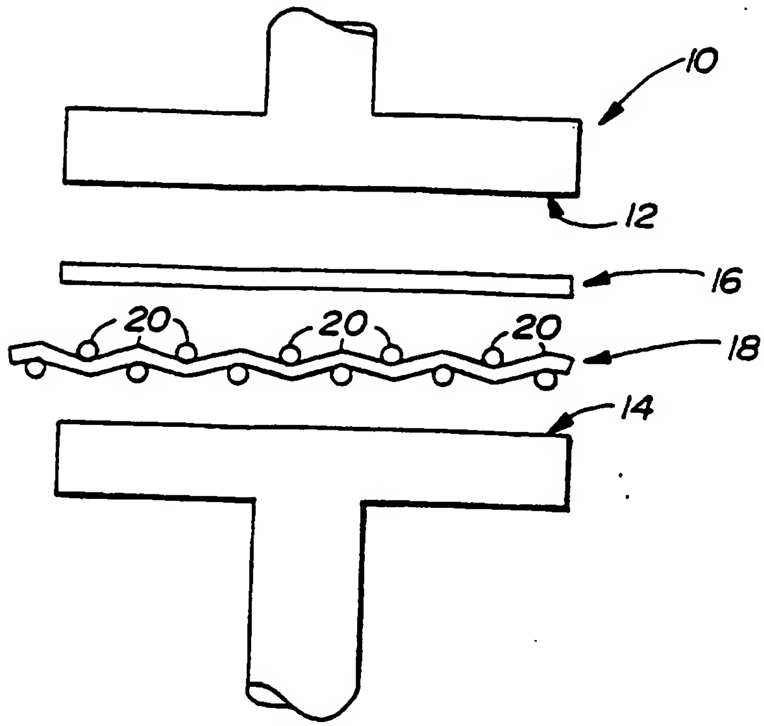


Fig-1

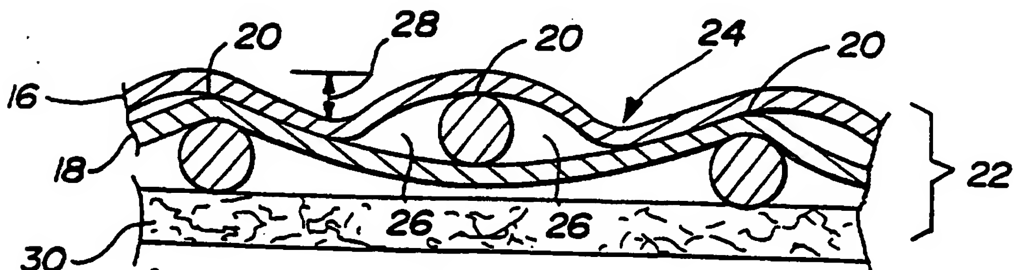


Fig-2

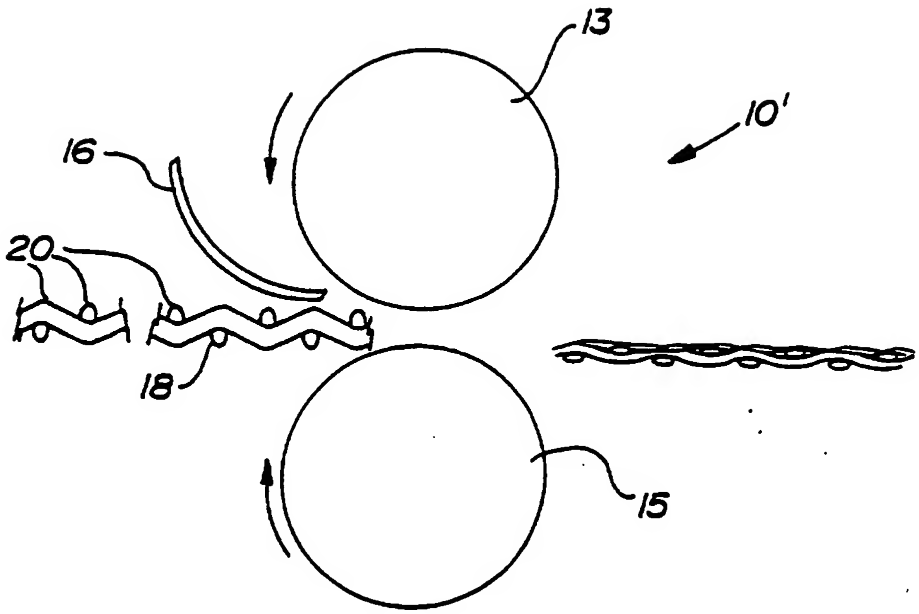


Fig-3

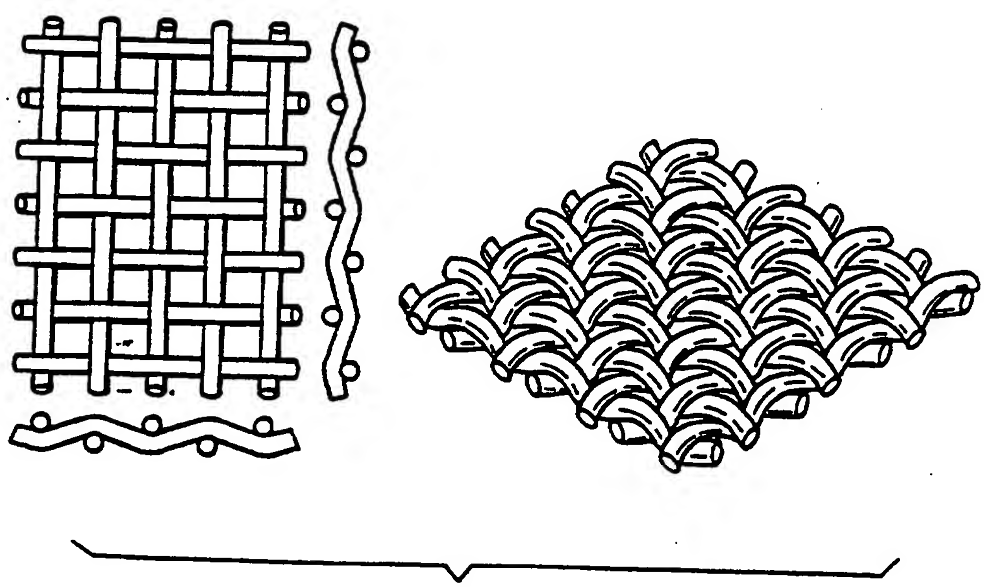

Fig-4A

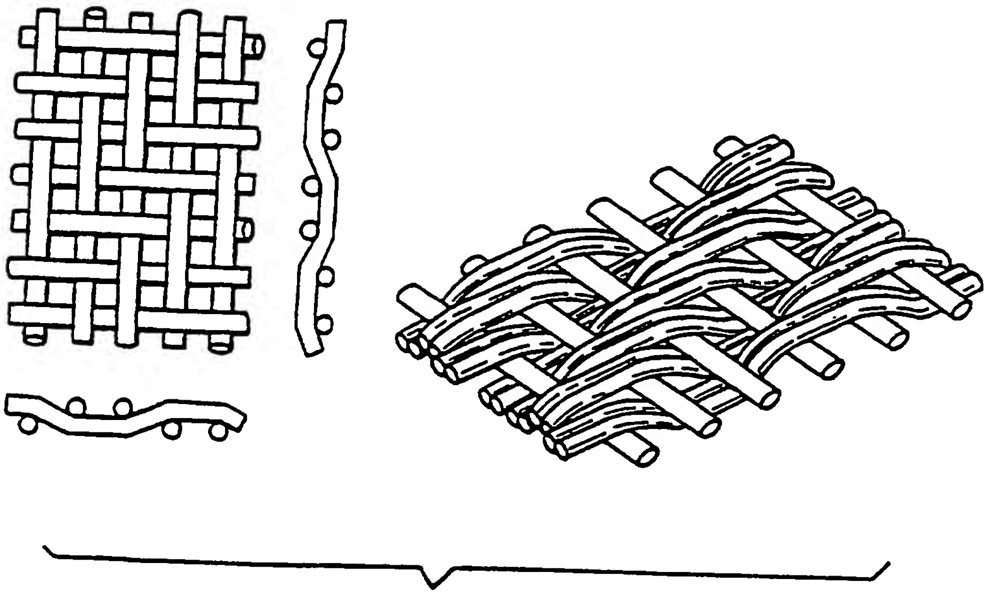

Fig-4B

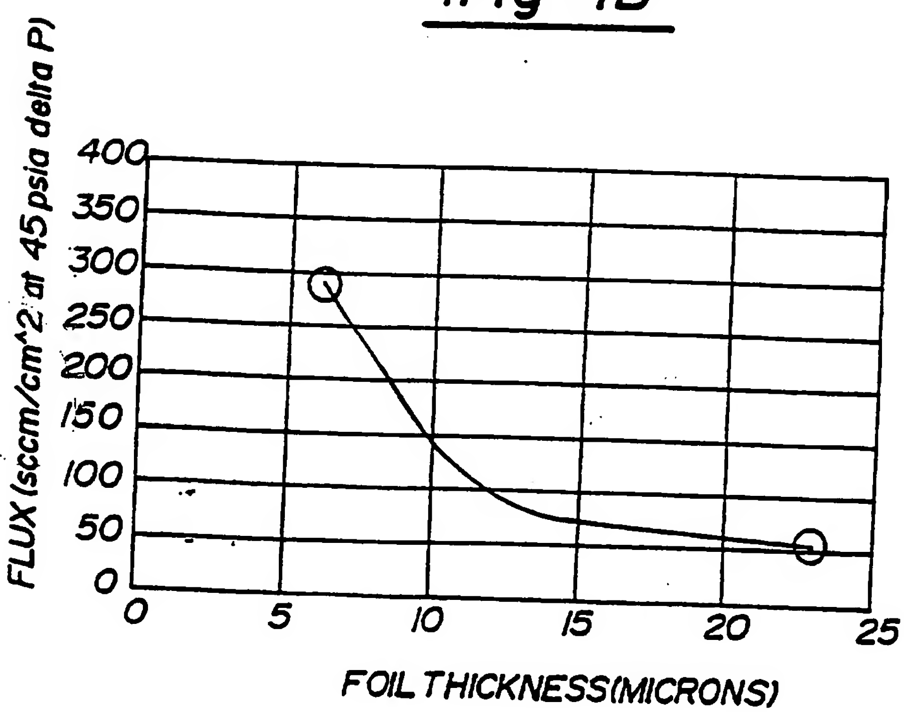
FLUX (sccm/cm^2 at 45 psia delta P)
400
350
300
250
200
150
100
50
0
0
5
10
15
20
25
FOIL THICKNESS(MICRONS)

Fig-5

# HYDROGEN SEPARATOR

The present invention is directed to a hydrogen separator and its method of manufacture. More specifically, the invention is directed to a hydrogen separator made from a thin foil secured to a support structure having an undulating surface.

Hydrogen separators are used in a number of commercial applications, including the refining of hydrocarbons, chemical processing, manufacture of hydrogenated oils as well as fuel cells. The separators work to refine a stream of relatively impure mixed gas containing less than 100% hydrogen (typically in the range of 20-80%) into very pure hydrogen (99.999%). Most common hydrogen separators use a thick palladium, palladium alloy, or composite of a group Vb metal coated with palladium or a palladium alloy. These common foils usually have a thickness of greater than 25 microns. The foil is produced by rolling or pressing ingots into sequentially thinner sheets. The practical limit of the rolling process is currently 25 microns. This is considered thick foil. The thick foil is supported by a method that allows the feed side pressure to be higher than the permeate pressure since the 25 micron foil is not capable of withstanding high pressure alone. One example of this construction is illustrated in US patent No. 5645626.

In systems that use a thick palladium or palladium alloy, the performance is such that cost and size are major barriers to automotive/commercial separator design. For coated group Vb metals cost, performance and size are acceptable, however the coated Group Vb metal substrates form hydrides that cause embrittlement resulting in unacceptable cycle life. An example of this construction is illustrated in US Patent No. 5738708. Furthermore, the coatings (~5000 Angstroms palladium) will interdiffuse during even limited, <100 hours, operation at above 400° C causing failure of the catalytic dissociation of $H_2$ into H at the surface.

The hydrogen disassociates on the foil surface and forms a metal hydride with the foil. The proton and electron from the hydrogen atom migrate through the foil and recombine on the opposite surface to form hydrogen gas. This method is illustrated in U.S. Patent No. 5645626.

The foil generally expands up to 20% when exposed to hydrogen while the underlying support material remains constant. Consequently, the foil must be made relatively thick to provide the durability needed for cyclic exposure to hydrogen gas. Unfortunately, the ability to pass hydrogen through a foil is directly proportional to the thickness of the foil while the cost is exponentially proportional in the case of palladium based foils. Increasing the foil thickness significantly reduces hydrogen permeability; also known as flux capacity. Increasing foil thickness also increases the cost of the separator. Increasing the temperature or pressure of the gas increases the flux capacity; however, the increased temperatures and pressures will damage thinner foils (<15 microns).

Another type of hydrogen separator uses very thin layers of palladium between 0.1 and 0.5 microns thick. Because these very thin layers cannot be made self-supporting, they are plated onto a carrier. The carrier, generally vanadium, niobium, or tantalum, enables the disassociated hydrogen atom to pass through the separator. Another coating containing palladium, on the opposite surface of the separator, recombines the disassociated hydrogen atoms into gaseous hydrogen. An example of this construction is illustrated in U.S. Patent Nos. 5738708 and 5149420.

This construction has the dual advantages of providing a large flux capacity because the palladium foil is very thin, and also relatively low cost because very little palladium is used in the coating material. Unfortunately, the current base metallic (e.g. vanadium) carriers are susceptible to hydrogen embrittling. After several cycles, the vanadium intermediate layer suffers internal fatigue and

fractures which cause the separator to fail when cycled to operating conditions. Increased temperatures and gas pressures further exacerbate the embrittling process and reduce the life of the separator.

Another separator construction uses a thin coating of palladium on a ceramic substrate. The ceramic substrate is made to be porous to hydrogen and to receive the palladium coating. Because the coating is relatively thin, it has a high flux capacity and relatively low cost. Unfortunately, palladium coated ceramic substrates suffer from the same durability problems as the vanadium substrates. The ceramic substrate and palladium foil have vastly different coefficients of thermal expansion. Also, the ceramic cannot be made to have a uniform porosity throughout the surface of the substrate. Those areas having relatively larger porosity create a void bridged by the palladium coating/foil. The ceramic expands up to 50 percent more than the palladium foil. This often causes the foil to crack or tear in areas of coarser porosity. These small microtears in the palladium foil reduce the separator's ability to filter impurities from the source hydrogen stream.

In summary, the prior art systems for hydrogen separation are too costly and large, or not reliable due to cracking of the coated layers and/or substrates to be viable for automotive/commercial separation of large volumes of hydrogen.

According to the invention there is provided a gas separator comprising: a thin foil having a thickness between 3 and 15, and permeable to a selected gas ; and a support structure having an undulating surface, said surface having contact areas secured to and supporting said foil, whereby said foil conforms to said undulating surface.

The present invention attempts to provide a separator that has the high flux capacity and low cost of the thin foil devices together with the high temperature and high pressure durability of thick, non-embrittling foils.

A hydrogen separator embodying the invention includes a thin hydrogen permeable foil having a thickness between 3 and 15 microns. The foil is bonded to a support structure. The support structure is formed to have an undulating surface. The surface includes contact areas on which are secured the foil. The foil generally conforms to the undulating surface. The foil is only secured to the contact areas of the support structure; this enables the foil to move in three directions as it expands and contracts when exposed to the hydrogen source stream. The contact areas are spaced relatively closely in comparison to the foil thickness and enable the thin foil to withstand high pressures.

The foil, once integrated with the support, becomes thick enough to then reliable secure it to mounting surfaces used in keeping separate the high and low pressure sides. If a thin foil were just rested on a support it would usually tear at this securing point if not fully integrated with the support.

The foil generally takes on a convoluted, repeatable shape, matching the undulating surface of the separator. Common separators include mesh or wire screens. The convoluted surface of the foil is generally between 20 and 50% larger than the plan view area of the foil. Screens having a mesh between 200 and 635 squares per inch were found to be generally suitable for use as hydrogen separators.

The separators are manufactured by rolling a thin palladium containing foil between 3 and 15 microns. The foil is then secured to the support structure. A rolling or pressing process is found suitable to mechanically fasten the foil to the support structure along the contact areas. The foil generally conforms to the undulating surface of the screen. The screen imparts convolutions onto the foil and increases its surface area by 20% to 50%. The foil remains secured to the screen without tearing or folding.

The present invention will now be described further, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a cross-sectional view of a separator assembly being joined in a press;

Figure 2 is a cross-sectional view of a separator using a standard mesh screen;

Figure 3 is a cross-sectional view of a separator assembly being joined by a pair of rollers;

Figure 4A are various views of a standard screen;

Figure 4B are various views of a "dutch weave" screen; and

Figure 5 is a graph of thermal expansion for palladium foil plotted against hydrogen flow.

The invention will be illustrated and described as a hydrogen separator for use with a fuel cell. The invention is useful for any situation where a mixed gas stream containing hydrogen is separated into a relatively pure hydrogen stream. These and other devices and methods of operation are included within the invention described herein. The following items are a word list of the components described in the drawings and are reproduced to aid in understanding the invention:

Word list

10,10' press
12,14 press surfaces
13,15 rollers
16 foil
18 support structure
20 contact areas
22 separator
24 foil surface
26 mesh openings
28 deformation amplitude
30 aluminium cloth

The invention is designed to provide a low cost hydrogen separator that can withstand the rigors of automotive applications. The separator has an operating temperature range from between -40 to 600°C and is capable of withstanding pressures up to 25 bar. The invention utilises a lower cost, thin palladium or palladium alloy foil as a separator material. The thin foil has the dual advantages of increasing the capacity of the separator while reducing the material cost. The foil and its method of manufacture are described in a commonly assigned patent application titled "METHOD OF MANUFACTURING THIN METAL ALLOY FOILS", filed on even date herewith and incorporated herein by reference. The foil is imparted with a convoluted shape to increase the surface area and to provide a unique structure that is capable of expanding and contracting without tearing. A support structure made of non-embrittling material imparts the convoluted shape to the foil and serves to support the foil during operation.

Illustrated in Figure 1 is a press 10 that is used to fasten the foil and support structure together. The press 10 may be either hydraulically, pneumatically, or mechanically driven.

The press 10 includes two press surfaces 12, 14 that join the foil and substrate. A palladium foil 16 is placed between the press surfaces 12, 14. The foil is composed of palladium, palladium alloys that have been shown to not embrittle, or palladium coated non-embrittling metals such as a body centred cubic alloy. The foil has a thickness of 3-15 microns, with the preferred thickness in the range of 5-7 microns. Illustrated in Figure 3 is a roll press 10'. Rollers 13, 15 press the foil onto the support structure 18.

A support structure 18 is placed juxtaposed to the foil 16. The support structure has an undulating surface to provide a variety of contact areas 20 for attachment to the foil 16. The undulating surface of the foil forms a mechanical lock with the support. The contact areas 20 have a space therebetween so that the foil surface contacting

adjacent contact areas 20 forms convolutions. A readily available material that has the needed undulating surface is a wire or mesh screen (wire cloth) having a mesh opening between 2 and 20 microns before compaction and 1 to 12 microns after compaction. The screen may be fabricated from a material that is insensitive to hydrogen exposure such as stainless steel, hasteloy, monel, nickel, or other suitable material. Stainless steel was found to be particularly well suited for use as a support structure because it was non-embrittling, readily available, high strength, and low cost. The support structure 18 can be coated with a material to further isolate metallic interdiffusion between the screen and the foil such as alumina or titanium.

The foil 16 and the support structure 18 are placed between the press surfaces 12, 14 or rollers 13, 15 and the press 10 is moved to the closed position or the rollers 13, 15 are indexed. The press 10, 10' applies between 20 and 70 tons of force per square inch for a period of 1-5 seconds. The foil 16 is mechanically fastened to the support structure 18. When the pressure exceeds 60,000 psi, the palladium foil becomes coined and forms a mechanical bond to the support structure by interlocking with the screen gaps as they close during the deformation process.

The foil 16 and support structure 18 form a separator 22, as illustrated in Figure 3. The separator 22 includes the foil 16 and the support structure 18. The foil 16 and the support structure 18 are mechanically fastened at the contact areas 20 by the foregoing pressing process. The pressing process also causes a deformation in the foil surface 24. The foil surface 24 is pushed into the mesh openings 26. The deformation amplitude 28 creates a series of convolutions on the foil surface 24. The foil surface 24 increases between 20 and 50% as compared to the plan view area of the foil before the joining operation. The foil 16 is supported over the contact areas 20 to span the mesh openings. This span distance is approximately equal to the screen mesh size. The screen mesh size is selected to

support the foil 16 for a given operating pressure, temperature and foil thickness. Thinner foils and higher operating pressures or temperatures generally require a smaller mesh sizes.

The separator 22 is placed within a passage or chamber that receives a source gas stream that contains impure hydrogen. The source gas contacts the foil surface 24. Hydrogen within the source gas disassociates on the foil surface 24 and forms atomic hydrogen. The atomic hydrogen forms a metallic bond with the host Pd or Pd Alloy and passes through the foil 16 and reassociates on the opposite foil surface to form gaseous hydrogen. The gaseous hydrogen passes freely through an underlying support structure 18. Separators of this construction are capable of purifying a source stream containing 15-99% hydrogen to greater than 99.999% pure hydrogen.

The source stream is generally heated to between 200 and 600°C, preferably 450°C to facilitate catalysis and hydration of the hydrogen into the foil 16. Both the hydration and elevated temperature cause the foil 16 to expand and elongate between 10 and 30%. This expansion and elongation causes the deformation amplitude 28 to increase. The expansion and elongation of the foil 16 is accommodated within the mesh opening 26. The contact areas 20 remain relatively constant. The foil 16 is free to expand and contract without tearing or folding.

A wide variety of screens having different mesh openings and mesh configurations exist. An example of this construction is illustrated in Figure 4A and 4B. The screen in Figure 4b uses a "dutch weave" construction where vertical threads interlock pairs of horizontal thread. This provides a coarser mesh having a rectangular opening.

Illustrated in Figure 5 is a graph of the hydrogen flux capacity vs. the palladium foil thickness. Foils made by the present invention have a hydrogen flux capacity more than five times that of prior art thick foils.

## CLAIMS

1. A gas separator comprising:

a thin foil (16) having a thickness between 3 and 15, and permeable to a selected gas ; and

a support structure (18) having an undulating surface, said surface having contact areas secured to and supporting said foil (16), whereby said foil (16) conforms to said undulating surface.

2. A separator as claimed in claim 1, wherein said foil has a convoluted surface.

3. A separator as claimed in claim 2, wherein said foil convoluted surface area is between 20 and 50% greater than the plan view area of the foil.

4. A separator as claimed in claim 3, wherein said contact areas are spaced apart between 2 and 20 microns.

5. A separator as claimed in claim 1, wherein said foil contains between 10 and 100% palladium.

6. A separator as claimed in claim 1, wherein said support structure is a wire mesh screen.

7. A support structure as claimed in claim 6, wherein said screen has a mesh between 200 and 635 standard weave, and up to 1400 and 200 in alternate weaves.

8. A support structure as claimed in claim 1, wherein said support structure may have an interdiffusion barrier coating.

9. A support structure as claimed in claim 1, wherein said support structure is a stainless steel screen.

10. A support structure as claimed in claim 1, wherein said selected gas is hydrogen.

11. A hydrogen separator for use with a fuel cell reformer separating a mixed gas source containing impure hydrogen comprising:

a thin hydrogen permeable foil containing palladium having a thickness between 3 and 15 microns; and

a wire mesh screen having a mesh opening between 2 and 20 microns, said screen having a having an undulating surface, said undulating surface having contact areas secured to and supporting said foil, whereby said foil forms a convoluted surface conforming to said undulating surface, said convoluted surface having a surface area 30% greater than the plan view area of the foil.

12. A method of producing a hydrogen separator, comprising the steps of:

providing a hydrogen permeable foil and a support structure immune to hydrogen embrittlement, said support structure having an undulating surface;

pressing together said foil and said support structure;

attaching said support structure to contact areas of said foil; and

forming a convoluted surface of said foil.

13. A gas separator substantially as hereinbefore described with reference to the accompanying drawings.

14. A method of producing a gas separator substantially as hereinbefore described with reference to the accompanying drawings.

The Patent Office

INVESTOR IN PEOPLE

**Application No:** GB 0024423.6 **Examiner:** Richard Gregson
**Claims searched:** All **Date of search:** 19 January 2001

# Patents Act 1977
# Search Report under Section 17

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): B1L (LAE, LAF, LAG, LAH, LAJ)

Int Cl (Ed.7): B01D, C01B (3/50)

Other: Online: EPODOC, WPI, JAPIO

**Documents considered to be relevant:**

| Category | Identity of document and relevant passage | | Relevant to claims |
|---|---|---|---|
| Y | GB 1287584 A | (JOHNSON MATTHEY) - see abstract and ... in particular. | 9,10 |
| X,Y | EP 0718031 A | (BEND RESEARCH) - see diagrams and ... in particular. | X -1,2, 3,5,8,10 Y-9,11 |
| X,Y | WO 0027507 A | (FROST & KREUGER) - see abstract and ... in particular. | X - 1,8,10 at least. Y - 9,11 |
| X,Y | DE 19905638 C1 | (POSCHMANN) - see abstract in particular. | X -1,6,10 Y-11 |
| X,Y | US 4699637 A | (INIOTAKIS et al) - see diagrams and... in particular. | X -1,2,5-8,10. Y - 9,11 |
| X,Y | US 4589891 A | (INIOTAKIS) et al) - see diagrams and... in particular. | X -1-6,8,10 Y-9,11 |

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Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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